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Synthesis of Pyridine Derivatives by Reactions of α,β-Unsaturated Nitriles with 2-Oxo-cycloalkano Carbothioic Acid Anilides

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Summary. The tandem Michael addition-cyclization of 2-oxo-cycloalkane carbothioic acid anilides **1**–**3** to benzylidenemalononitrile **4** yielded spiroannulated pyridines **5**–**7**. Reaction of acrylonitrile with **2** and **3** gave 2,2-disubstituted Michael adducts **14**, **15**, whereas with **1** led to 2,2,5-tri(2-cyanoethyl)-cyclopentanone **11**.

Keywords. 2-Oxo-cycloalkano carbothioic acid anilides; 3-Pyridine-spiro-2′-cycloalkanone; α,β-Unsaturated nitriles.

Synthese von Pyridinderivaten durch Reaktionen von α,β-ungesättigten Nitrilen mit 2-Oxo-cycloalkano-thiokohlensäure-aniliden

Zusammenfassung. Die Michael Tandem-Addition-Cyclisierung von 2-Oxo-cycloalkano-thiokohlensäure-aniliden **1**–**3** mit Benzylidenmalononitril **4** ergab die spiroannelierten Pyridine **5**–**7**. Reaktion von Acrylnitril mit **2** und **3** ergab die 2,2-disubstituierten Michael-Addukte **14**, **15**, wohingegen mit **1** 2,2,5-Tri(2-cyanethyl)-cyclopentanon **11** erhalten wurde.

Introduction

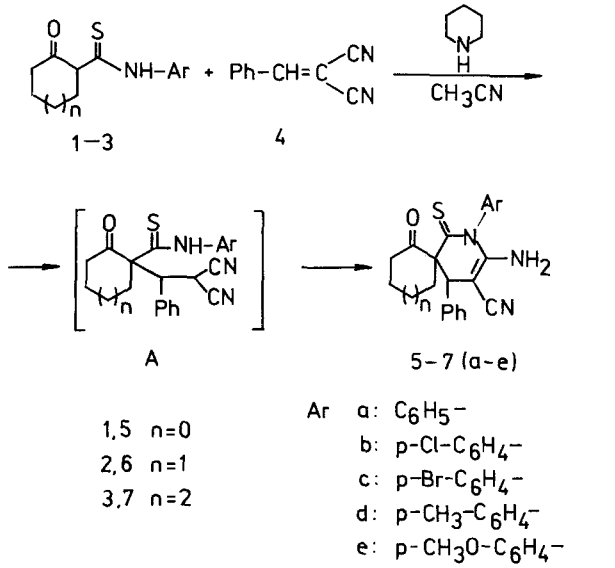
The synthesis and chemistry of polyfunctionalized pyridines have attracted considerable attention of many laboratories as they were found to be valuable precursors in the approach to a wide branch of natural products [1, 2] and due to their biological activity [3].

We have previously published [4, 5] the synthesis of enaminonitriles of fused cycloalkenopyridines, which involved the reaction of enamines of cyclic β-keto acid anilides with malononitrile. Another highly efficient synthetic route to polyfunctionalized pyridines [6], which has been developed by us, consists in tandem Michael addition cyclization of benzoylthioacetanilides to arylidenemalononitriles or ethyl 2-cyanocinnamates.

In this study the reactions of 2-oxo-cycloalkano carbothioic acid anilides containing five- (**1**), six- (**2**) and seven- (**3**) membered rings with benzylidenemalononitrile **4** and acrylonitrile **10** are reported.

Results and Discussion

The reaction of the appropriate thioanilides **1–3** with benzylidenemalononitrile **4**, carried out in the boiling acetonitrile solution in the presence of piperidine as a catalyst, gave yellow coloured products **5–7** in moderate to good yields (Table 1, Scheme 1).



Scheme 1

According to the reference reports [7, 8] as well as our experiences [6] the Michael addition of **1–3** to **4** is assumed to be the first step of these reactions. There are three acidic centers in each molecule of **1–3**, which are able to participate in an addition to **4**. The strongest acidity reveals the hydrogen atom attached to C-1, due to the influence of the neighboring carbonyl and thiocarbamyl groups. Thus the Michael addition of **1–3** to **4** leads to formation of adducts **A** as the intermediates (Scheme 1). The further ring closure of these intermediates is dependent on the presence of a compatible functionality at the proper position within the molecules and on the reaction condition. In the investigated reactions the intermediate adducts **A** were not isolated, since after their formation, they immediately underwent intramolecular cyclization resulting in compounds **5–7**.

In order to confirm the assumption that the intermediate Michael adducts were formed exclusively by nucleophilic attack of carboanion at C-1 of thioanilides **1–3** on **4**, we carried out the analogous reaction of **4** with 1-oxo-indano-2-carbothioic acid anilide **8** [9]. Compound **8** contains only one acidic hydrogen atom at carbon C-2. The reaction of **4** with **8** performed under the same conditions gave yellow coloured product **9** (Scheme 2). Its IR spectrum was similar to those of compounds **5–7** (Table 1). It displayed a strong stretching absorption at 1706 cm^{-1} (CO), 2186 cm^{-1} (CN), and three bands at 3320–3480 cm^{-1} (NH_2). The most valuable for structure elucidation was the ^{1}H-NMR spectrum of **9**. It revealed the multiplet of 14 aromatic protons at $\delta = 7.2$–7.7 ppm, two singlets at $\delta = 4.4$ ppm and $\delta = 3.8$ ppm of two protons of NH_2, and one proton at C-4 of the pyridine ring.

At $\delta = 3.19$ ppm ($J = 17.8$ Hz) and $\delta = 4.39$ ppm ($J = 17.8$ Hz) there was observed a pair of doublets each integrating for one proton. These four lines can only be assigned to the diastereotopic CH_2 protons of the indene moiety. Such a pattern is consistent only with the spiro junction between two rings in **9**. Taking into account the similarities of physical and chemical properties of **9** with those of **5**–**7**, the structure 6-amino-4-aryl-5-cyano-1-phenyl-2-thioxo-1,2,3,4-tetrahydropyridine-3-spiro-2′-cycloalkanone was assigned for all obtained compounds **5**–**7**.

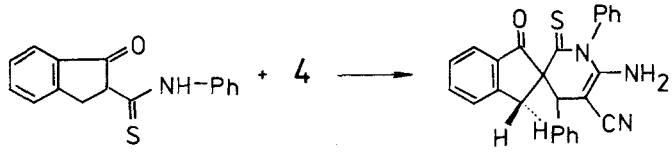
Next we studied the reaction of **1**–**3** with other Michael acceptors e.g. acrylonitrile, cinnamononitrile, and ethyl 2-cyanocinnamate expecting formation of similar spiroannulated derivatives of pyridine. Among these α-β-unsaturated nitriles only acrylonitrile **10** reacted with **1**–**3** under our conditions.

The reaction of **1** with **10** carried out in acetonitrile in the presence of anhydrous potassium carbonate furnished adduct **11** [10], which was confirmed by analytical and spectral data. Compound **11** was formed by successive reactions of **1** with three molecules of **10** and elimination of phenylisothiocyanate (Scheme 3).

In contrast to **1**, compounds **2** and **3** reacted with the same excess of **10** only in 1:1 molar ratio to give the corresponding adducts. The IR spectra of both compounds revealed the bands of CN and NH groups, that suggested a noncyclic structure for these Michael adducts.

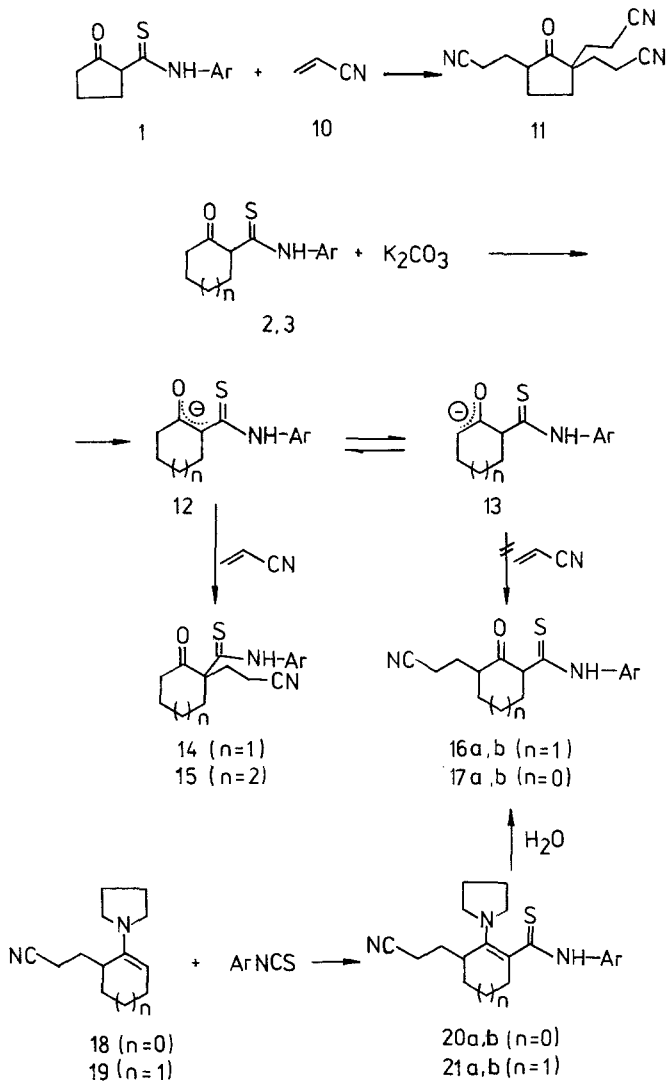
Reaction of **2** with **10** in the presence of potassium carbonate proceeds via enolate anion [11] **12** or **13**, and addition of acrylonitrile may lead to products **14** or **16** (Scheme 3). Since the complex pattern of the aliphatic resonances in the ^{1}H-NMR spectrum did not allow to establish the structure of the obtained product, we accomplished this by a chemical method. Our approach based on the assumption that enolate anions of 2-substituted cyclohexanone exist mainly as more substituted **12** [11], whereas less substituted isomers predominate as their pyrrolidine enamines **19** [12–14]. So the reaction between 3-(2-cyanoethyl)-2-pyrrolidine-1-cyclohexene (**19**) [14] with phenylisothiocyanate was performed. The product of this reaction, **21**, rapidly hydrolyzed under the influence of methanol or moisture to ketone **16a**. Analytical, MS, and IR data proved that the compound obtained in these two reactions was an isomeric disubstituted cyclohexanone. Moreover, the ^{1}H-NMR spectrum of the product obtained via the enamine procedure showed a triplet at $\delta = 3.95$ ppm integrating for one proton adjacent to carbonyl and thiocarbonyl groups, allowing the attribution of structure **16** to this compound. 2,2-Disubstituted cycloalkanones **14**, **15** were thereby obtained in the reaction between **2** or **3** and **10** (Scheme 3).

Enamine **18** gave relatively stable adducts **20**. They underwent hydrolysis in acidic medium to **17**. Their IR and ^{1}H-NMR spectra taken in $CDCl_3$ suggested



8 9

Scheme 2

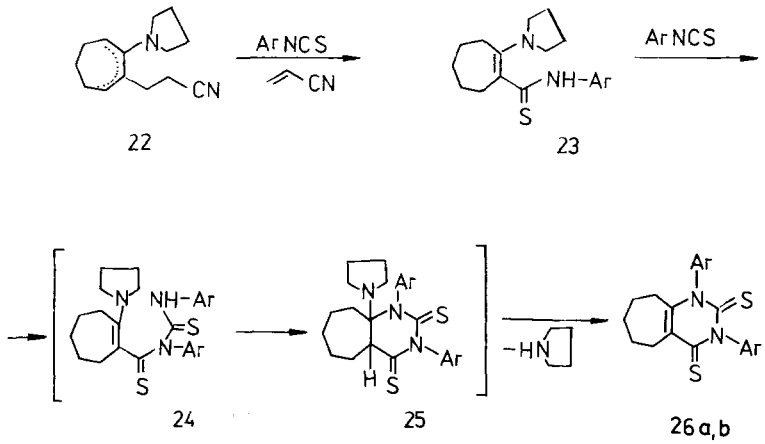


Scheme 3

that the keto-enol equilibrium for these compounds is strongly shifted towards enolic forms (Table 1).

The reaction of **22** with arylisothiocyanates (Scheme 3) took an unexpected course and led to **26**. The IR spectra of **26** showed neither CN nor NH absorptions. Contrary to **20** or **21**, compound **26** was resistant towards acidic or alkaline hydrolysis. The same product (**26a**) was also obtained in the reaction of 1-pyrrolidine-1-cycloheptene with phenylisothiocyanate. Combining the above data with results of elemental analysis and MS spectra the cyclohepta-pyrimidine structure was assigned for products **26**.

These results can be attributed to the unstable nature of **22**, which reacting with arylisothiocyanates easily eliminates acrylonitrile, thereby furnishing adduct **23**. Addition of **23** to a second molecule of arylisothiocyanate followed by cyclization



Scheme 4

and elimination of pyrrolidine leads to **26** (Scheme 4). The suggested mechanism is similar to the one reported earlier [15].

Considering the above results, the question arises why **14** and **15**, containing both cyanoethyl and thiocarbamoyl groups attached to the same carbon atom, do not undergo intramolecular cyclization to pyridine. This can be explained by comparison of the effects of substituents in the intermediate **A** (Scheme 1) and in **14** or **15** (Scheme 3). Namely, cyano and phenyl substituents decrease the electron density at the nitrile carbon atom in **A** whereas the methylene group in **14** and **15** exhibits an opposite effect causing nucleophilic attack of the electron lone pair of amido nitrogen atom on nitrile carbon to be less effective. Moreover, the steric position of the cyano and amino functions can also be less preferable for intramolecular cyclization.

Experimental Part

All melting points were determined on a Boetius hot stage apparatus and are therefore corrected. Infrared spectra were recorded on a IR 75 Specord and 85 Specord (Zeiss, Jena) spectrometer in nujol and in HCB mulls. ^{1}H-NMR spectra were taken at 100.0 MHz for deuterochloroform or *DMSO-d_6* solution with a Tesla BS 567A spectrometer. Chemical shifts were referenced to $SiMe_4$ as internal standard. Mass spectra were obtained with a Jeol IMS-D100 or LKB 9000S spectrometer. Elemental analyses were carried out with a Perkin Elmer 240 instrument.

2-Oxo-cycloalkane-carbothioic acid anilides **1–3** [16, 17] and benzylidenemalononitrile [18] **4** were prepared according to reference procedures. Silica gel 60 Fluka was used for column chromatography.

6-Amino-1-aryl-5-cyano-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyridine-3-spiro-2'-cycloalkanones (**5–7, 9**) (*General Procedure*)

A mixture of equimolar amounts of appropriate thioanilide **1–3** or **8** (0.01 mol) and benzylidenemalononitrile **4** (0.01 mol) was refluxed in 100 ml of acetonitrile with a few drops of piperidine for 4 h. Evaporation of solvent gave an orange semisolid product, which was treated with methanol and cooled. The precipitate was filtered off and recrystallized from acetic acid or acetonitrile.

Table 1. Yields, physical properties, elemental analysis, and spectroscopic data of compounds obtained

	Yield [%]	M.p. [°C]	Empirical formula mol. mass[a]	Analysis calcd. (found) C	H	N	S	IR [cm^{-1}]	^{1}H-NMR (δ/ppm)
5a	49	169	$C_{22}H_{19}N_3OS$ 373.5 (373.1)	70.75 (71.05)	5.13 (5.64)	11.25 (11.36)	8.58 (8.30)	3440, 3340 (NH), 2190 (CN), 1730 (CO)	1.74–2.86 (m, 6H, CH_2), 3.97 (s, 1H, CH), 5.72 (s, 2H, NH_2), 7.13–7.55 (m, 10H, aromatic H)
5b	32	237–238	$C_{22}H_{18}ClN_3OS$ 407.9 (407.4)	67.77 (67.81)	4.44 (5.08)	10.30 (10.51)	7.86 (7.84)	3420, 3330 (NH), 2200 (CN), 1730 (CO)	1.57–2.93 (m, 6H, CH_2), 3.96 (s, 1H, CH), 5.97 (s, 2H, NH_2), 7.13–7.67 (m, 9H, aromatic H)
5c	52	235–237	$C_{22}H_{18}BrN_3OS$ 452.4 (452)	58.41 (58.25)	4.01 (4.39)	9.29 (9.32)	7.09 (7.10)	3420, 3350 (NH), 2190 (CN), 1730 (CO)	1.81–2.95 (m, 6H, CH_2), 3.73 (s, 1H, CH), 4.27 (s, 2H, NH_2), 7.12–7.75 (m, 9H, aromatic H)
5d	69	245–246	$C_{23}H_{21}N_3OS$ 387.5 (387.3)	71.28 (70.83)	5.46 (5.44)	10.84 (10.94)	8.27 (8.50)	3430, 3320 (NH), 2180 (CN), 1730 (CO)	1.74–2.94 (m), and 2.41 (s, 9H, CH_2, CH_3); 3.95 (s, 1H, CH), 5.69 (s, 2H, NH_2), 7.02–7.53 (m, 9H, aromatic H)
5e	57	236–237	$C_{23}H_{21}N_3O_2S$ 403.5 (403.1)	68.46 (68.87)	5.24 (5.27)	10.41 (10.70)	7.94 (7.64)	3430, 3330 (NH), 2180 (CN), 1730 (CO)	1.74–2.86 (m, 6H, CH_2), 3.84 (s, 3H, OCH_3), 3.94 (s, 1H, CH), 5.75 (s, 2H, NH_2), 7.08–7.51 (m, 9H, aromatic H)
6a	39	252–253	$C_{23}H_{21}N_3OS$ 387.5 (387)	71.28 (71.45)	5.46 (5.27)	10.84 (10.98)	8.27 (8.33)	3480, 3350 (NH), 2180 (CN), 1700 (CO)	1.38–2.36 (m, 8H, CH_2), 4.45 (s, 1H, CH), 5.75 (s, 2H, NH_2), 7.30–7.53 (m, 10H, aromatic H)

6b	45	263–265	$C_{23}H_{20}ClN_3OS$ 421.9 (421)	65.47 (65.42)	4.78 (5.20)	9.96 (10.29)	7.59 (7.59)	3440, 3320 (NH), 2180 (CN), 1690 (CO)	1.38–2.35 (m, 8H, CH_2), 4.55 (s, 1H, CH), 6.12 (s, 2H, NH_2), 7.38–7.70 (m, 9H, aromatic H)
6c	36	257–258	$C_{23}H_{20}BrN_3OS$ 466.4 (466)	59.23 (58.96)	4.32 (4.74)	9.01 (9.07)	6.87 (6.44)	3440, 3330 (NH), 2180 (CN), 1690 (CO)	1.25–3.16 (m, 8H, CH_2), 4.21 (s, 1H, CH), 4.31 (s, 2H, NH_2), 7.31–7.76 (m, 9H, aromatic H)
6d	25	271–273	$C_{24}H_{23}N_3OS$ 401.5 (401)	71.79 (71.19)	5.77 (5.03)	10.47 (10.56)	7.98 (8.11)	3450, 3350 (NH), 2180 (CN), 1710 (CO)	1.38–2.41 (m), 1.93 (s, 11H, CH_2, CH_3), 4.54 (s, 1H, CH), 5.82 (s, 2H, NH_2), 7.13–7.45 (m, 9H, aromatic H)
6e	14	260–262	$C_{24}H_{23}N_3O_2S$ 417.5 (417)	69.03 (68.93)	5.55 (5.88)	10.06 (10.05)	7.67 (7.69)	3440, 3330 (NH), 2180 (CN), 1700 (CO)	1.38–2.51 (m, 8H, CH_2), 3.84 (s, 3H, OCH_3), 4.53 (s, 1H, CH), 5.87 (s, 2H, NH_2), 7.13–7.38 (s, 9H, aromatic H)
7a	43	247–248	$C_{24}H_{23}N_3OS$ 401.5 (401)	71.79 (71.46)	5.77 (5.54)	10.47 (10.84)	7.98 (7.57)	3450, 3320 (NH), 2190 (CN), 1695 (CO)	1.25–2.60 (m, 8H, CH_2), 3.05 (t, 2H, CH_2), 3.87 (s, 1H, CH), 4.29 4.29 (s, 2H, NH_2), 7.26–7.59 (m, 10H, aromatic H)
7b	37	255–257	$C_{24}H_{22}ClN_3OS$ 436.0 (435)	66.12 (66.26)	5.09 (5.47)	9.64 (10.21)	7.35 (7.47)	3430, 3330 (NH), 2180 (CN), 1695 (CO)	1.25–2.60 (m, 8H, CH_2), 3.04 (t, 2H, CH_2), 3.86 (s, 1H, CH); 4.23 (s, 2H, NH_2), 7.16–7.60 (m, 9H, aromatic H)

Table 1 (continued)

	Yield [%]	M.p. [°C]	Empirical formula mol. mass[a]	Analysis calcd. (found) C	H	N	S	IR [cm^{-1}]	^{1}H-NMR (δ/ppm)
7c	17	256–257	$C_{24}H_{22}BrN_3OS$ 480.4 (479)	60.00 (60.37)	4.62 (5.27)	8.75 (8.61)	6.67 (6.65)	3430, 3330 (NH), 2180 (CN), 1690 (CO)	1.25–2.65 (m, 8H, CH_2), 3.14 (t, 2H, CH_2), 3.85 (s, 1H, CH), 4.44 (s, 2H, NH_2), 7.30–7.85 (m, 9H, aromatic H)
7d	43	276–277	$C_{25}H_{25}N_3OS$ 415.5 (415)	72.26 (72.53)	6.06 (6.33)	10.14 (10.35)	7.72 (7.67)	3440, 3320 (NH), 2180 (CN), 1695 (CO)	1.25–2.60 (m), 2.45 (s, 11H, CH_2, CH_3), 3.05 (t, 2H, CH_2), 3.87 (s, 1H, CH), 4.27 (s, 2H, NH_2), 7.20–7.55 (m, 9H, aromatic H)
7e	28	267–269	$C_{25}H_{25}N_3O_2S$ 431.6 (431)	69.58 (69.76)	5.84 (5.75)	9.74 (9.36)	7.43 (7.57)	3430, 3330 (NH), 2180 (CN), 1696 (CO)	1.25–3.15 (m, 10H. CH_2), 3.88 (s, 4H, CH_3, CH), 4.28 (s, 2H, NH_2), 7.10–7.57 (m, 9H, aromatic H)
9	24	237–240	$C_{26}H_{19}N_3OS$ 421.5 (421)	74.08 (74.69)	4.54 (4.44)	9.97 (9.95)	7.61 (7.53)	3480 3320 (NH), 2186 (CN), 1706 (CO)	3.19 (d, J = 17.8Hz, 1H), 4.39 (d, J = 17.8Hz, 1H), 3.80 (s, 1H, CH), 4.40 (s, 2H, NH_2), 7.20–7.80 (m, 14H, aromatic H)
11	26	178–179	$C_{14}H_{17}N_3O$ 243.3 (243)	69.11 (68.59)	7.04 (7.00)	17.27 (17.78)		2248 (CN), 1732 (CO)	1.88–2.45 (m, 16H CH_2)
14	21	145–146	$C_{16}H_{18}N_2OS$ 286.4 (286)	67.10 (66.73)	6.34 (6.09)	9.78 (9.60)	11.19 (11.89)	3246 (NH), 2246 (CN), 1706 (CO)	1.78–2.86 (m.12H.CH_2), 7.34–7.63 (m, 5H, aromatic H), 9.34 (s, 1H, NH)
15	57	152–154	$C_{17}H_{20}N_2OS$ 300.4 (300)	67.97 (68.45)	6.71 (6.81)	9.32 (9.25)	10.67 (10.87)	3250 (NH), 2240 (CN), 1700 (CO)	1.70–2.83 (m, 14H, CH_2), 7.34–7.62 (m, 5H, aromatic H), 9.87 (s, 1H, NH)

16a	65	191–194	$C_{16}H_{18}N_2OS$ 286.4 (286)	67.10 (67.18)	6.34 (6.31)	9.78 (9.51)	11.19 (11.16)	3216 (NH), 2248 (CN), 1704 (CO)	1.53–1.97 (m, 11H, CH_2, CH), 3.95 (t, 1H, CH), 7.30–7.90 5H, aromatic H), 11.3 (s, 1H, NH).
16b	60	180–183	$C_{16}H_{17}ClN_2OS$ 320.8 (320)	59.89 (59.97)	5.34 (5.39)	8.73 (8.40)	9.99 (9.91)	3224 (NH), 2240 (CN), 1712 (CO)	1.40–2.36 (m, 11H, CH_2, CH), 4.00 (t, 1H, CH), 7.50–8.10 (d of d, 4H, aromatic H), 11.50 (s, 1H, NH)
17a	15	100–102	$C_{15}H_{16}N_2OS$ 272.4 (272)	66.15 (66.31)	5.92 (5.81)	10.29 (10.06)	11.77 (11.91)	3319 (NH), 2247 (CN), 1605 (CO)	1.45–2.40 (m, 4H, 2 CH_2), 2.50–2.75 (two t, 4H, 2 CH_2), 2.80–3.15 (m, 1H, CH), 7.35–8.0 (m, 6H, aromatic H and NH), 13.85 (s, 1H, OH enol)
17b	13	118–120	$C_{15}H_{15}ClN_2OS$ 306.8 (306)	58.72 (58.90)	4.92 (4.89)	9.13 (8.64)	10.45 (10.31)	3136 (NH), 2248 (CN), 1600 (CO)	1.50–2.37 (m, 4H, 2 CH_2), 2.48–2.74 (two t, 4H, 2 CH_2), 2.85–3.2 (m, 1H, CH), 7.30–7.85 (m, 5H, aromatic H and NH), 13.79 (s, 1H, OH enol)
26a	66	228–230	$C_{21}H_{20}N_2S_2$ 364.5 (364)	69.19 (69.29)	5.53 (5.98)	7.68 (8.00)	17.59 (17.97)	1687 (C=C)	1.35–1.90 (m, 6H, CH_2), 2.25–2.55 (m, 2H, CH_2), 3.05–3.35 (m, 2H, CH_2), 7.10–7.63 (m, 10H, aromatic H)
26b	81	274–276	$C_{21}H_{18}Cl_2N_2S_2$ 433.4 (432)	58.19 (58.32)	4.19 (4.11)	6.46 (6.49)	14.80 (14.23)	1585 (C=C)	1.30–1.95 (m, 6H, CH_2), 2.25–2.55 (m, 2H, CH_2), 3.1–3.4 (m, 2H, CH_2), 7.15–7.69 (m, 8H, aromatic H)

[a] M^+ values found by mass spectrometry in parentheses

Reaction of Thioanilides **2**, **3** *with Acrylonitrile*
2-Oxo-cycloalkane-1-(2-cyanoethyl)-carbothioic Acid Anilides (**14**, **15**)

A mixture of appropriate thioanilide **2** or **3** (0.01 mol) and acrylonitrile **10** (0.03 mol) was refluxed in 100 ml of acetonitrile with anhydrous potassium carbonate (1 g) until starting thioanilide disappeared (TLC control). After cooling, potassium carbonate was filtered off. Evaporation of solvent gave a yellow oil, which was purified by column chromatography on silica gel using chloroform as eluent; pale yellow prisms from methanol.

2,2,5-Tri(2-cyanoethyl)-cyclopentanone (**11**)

Reaction of **1** (0.01 mol) with **10** (0.03 mol) in acetonitrile in the presence of potassium carbonate gave **11** as the sole product in 26% yield. Colorless prisms from methanol, m.p. 177–179 °C (Ref. [10] 178–179 °C).

Reaction of Arylisothiocyanates with 3-(2-Cyanoethyl)-2-pyrrolidine-1-cycloalkenes (**16**, **17**)

An equimolar mixture of the appropriate arylisothiocyanate (0.05 mol) and enamine **18** or **19** (0.05 mol) and a few drops of triethylamine in 100 ml of chloroform was refluxed for 1 h. The solvent was evaporated and the orange resinous residue was treated with methanol. The precipitate (**20**, **21**), was filtered off and recrystallized from methanol. Compounds **21** hydrolized during recrystallization to ketone **16**. Enamines **20a**, **b** were hydrolyzed in aqueous solution by treating with dilute hydrochloric acid. The water solution was extracted with dichloromethane, which was then dried over anhydrous sodium sulphate. Evaporation of solvent gave an oily product, which was purified by column chromatography on silica gel in chloroform and recrystallized from methanol.

1,3-Diaryl-2,3,6,7,8,9-hexahydro-5H-cyclohepta[d]pyrimidine-2,4-dithione (**26**)

The reaction was carried out in a similar way as with enamines **18** or **19**. Enamine **22** (0.02 mol) and arylisothiocyanate (0.02 mol) refluxed in 50 ml of chloroform for 1.5 h yielded **26a**, **b**.

Compound **26a** was also obtained in reaction of 1-pyrrolidine-1-cycloheptene and phenylisothiocyanate under the same reaction conditions.

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